BAND SPECTRUM OF CADMIUM BROMIDE

By C. RAMASASTRY

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Plates XXIIA and B

ABSTRACT. The H. F. emission spectrum of cadmium bromide molecule is reinvestigated *P*, *Q* component head splitting is presented for the (0, 0) and (1, 1) bands of the main system and a few additional bands are assigned to this system. A new group of bands is interpreted as forming the counterpart of the main system which arises from $^2\Pi - {}^2\Sigma$ transition. About 50 bands are measured in the visible region and regularities shown.

INTRODUCTION

In the early work of Walter and Barratt (1929) on the absorption spectra associated with various compounds of zinc, cadmium and mercury, about 12 bands were listed in the region $\lambda 3551$ to $\lambda 3407$ as belonging to (Cd + Br). But the wavelengths of these bands agree closely with the TlBr absorption band heads obtained later by Butkow (1931) and so the bands are considered by Pearse and Gaydon (1941) as really belonging to TlBr but not to Cd Br. Recent investigations of Oeser (1935) on the absorption and fluorescent spectra of the halides of zinc and cadmium did not reveal any discrete bands of the CdBr molecule. The high frequency emission spectrum of cadmium bromide vapour was studied by Wieland (1929) who analysed a system of violet degraded bands of high intensity, lying in the region $\lambda\lambda 3250 - 3120$, as consisting of six sequences with the (0, 0) band placed at $\lambda 3176.65$, $\nu\ 31470.5$. He also listed three unclassified bands at $\lambda 3395.1(3)$, $3092.5(1)$, $3075.4(0)$. The existence of diffuse bands in the visible region from $\lambda 6400 - \lambda 3300$ was just mentioned by him but no measurements were given. Howell (1943) considered, from an analogy with the band systems of the other halide molecules of Zn, Cd, and Hg, that the system analysed by Wieland should be one of the components of $^2\Pi - {}^2\Sigma$ transition; but the other component system could not be established. The present work is taken up with a view to finding out this missing component system and to search for other band systems of CdBr which would correspond to the various known systems of the related molecules.

EXPERIMENTAL

The discharge tube is of thick-walled pyrex glass with external electrodes, the source of excitation being a H. F. oscillator constructed by the

author. Heating is done by an etna burner until the colour of the discharge becomes intense white. Ilford Selo chrome and Special rapid plates are employed for photographing the bands. Preliminary investigation is carried out with Hilger small and medium quartz spectrographs using plates sensitised for the far ultra-violet.

RESULTS

(*a*) No bands are obtained in the region $\lambda 3000 - \lambda 1850$ but four broad and ill-defined continua are recorded extending over regions (*i*) $\lambda\lambda 2500 - 2550$ (*ii*) $\lambda\lambda 2610 - 2660$ (*iii*) $\lambda\lambda 2700 - 2785$ and (*iv*) $\lambda\lambda 2875 - 2930$.

(*b*) The visible bands, clearly red-degraded, occur in the region $\lambda 4000 - \lambda 3850$. Of these, those lying between $\lambda 4100$ $\lambda 4000$ are of greater intensity than the rest. There is also a strong general continuum overlying the visible bands. This continuum gradually fades away to shorter wavelengths and is practically imperceptible at about $\lambda 3350$.

(*c*) An isolated violet degraded band at $\lambda 3295.1$ and another faint band at $\lambda 3324$, obviously related to the former, could be definitely observed.

(*d*) The Wieland system occurs in the region $\lambda 3250 - \lambda 3100$. This consists of the most intense bands of the entire spectrum.

(*e*) A few faint bands in the $\lambda 3000$ region could be detected in the rotational structure of the OH band, $\lambda 3064$.

SYSTEM *D*

Wieland's system (system *D*.) is photographed by the author on the Hilger quartz Littrow spectrograph. Lighter exposures showed that the (0, 0) and (1, 1) bands are split up into two component heads (Plate XXIIA, Fig. *a*). Such double heads are not observed for any of the remaining bands of the system. Hence the above components cannot be due to bromine isotope effect but are to be considered as *P* and *Q* heads. Details of measurements are given below :

TABLE 1

(v', v'')	ν Wieland	ν Author	$\Delta\nu$
0, 0	31170.8	31170.7	3.2
		31173.9	
1, 1	31491.0	31493.4	2.8
		31496.2	

The number of component heads observed in each band gives the conclusive evidence for the consideration that the system is due to $^2\Pi - {}^2\Sigma$ transition. Then the other component system should also be present, from the analogy of the spectra of the corresponding molecules. The three unclassified bands of Wieland in the $\lambda 3095$ region cannot form the missing component system, for (*i*) they give 840 cm^{-1} for the $^2\Pi$ width which is too small compared with the expected value of 1140 cm^{-1} derived from the ^2P separation of the Cd atom (*ii*) there are no regularities among the bands In the region of these faint bands listed by Wieland, a few more bands also could be measured in the present work ; the presence of a band is suspected wherever there is a shading of the rotational lines of the OH band (Plate XXIIA, Fig. *b*). This fragmentary group can be interpreted as forming the higher members of the Wieland system and the bands are classified accordingly in Table II.

TABLE II

Additional Bands in the *D*-system of CdBr

Wieland λ (Int.)	Author λ (Int.)	ν_{obs}	ν_{cal}	(v', v'')
3095.1(3)	3095.0(3)	32301	32299.3	(7, 4)
3091.5(1)		32337	32334.3	(9, 6)
	3089.7(0)	32388	32389.2	(12, 9)
3075.1(0)	3075.6(1)	32505	32508.8	(6, 2)
	3072.0(0)	32536	32536.1	(7, 3)
			32543.3	(8, 4)
	3068.1(0)	32583	32571.1	(10, 6)
			32591.3	(11, 7)
	3061.1(0)	32657	32658.1	(13, 9)

The positions of the various bands is calculated with the help of the formula

$$\nu = 31458.3 + 254.5(n' + \tfrac{1}{2}) - 230.0(n'' + \tfrac{1}{2})$$
$$0.75(n' + \tfrac{1}{2})^2 + 0.50(n'' + \tfrac{1}{2})^2$$

which was derived by Wieland (1930) to represent the *D*-system. The above bands form a continuation of the intensity parabola when arranged in a Deslandre's table, thus supporting their positions in the vibrational scheme.

SYSTEM *C*

With the bands on the short wavelength side of the *D*-system having been classified as above, the only alternative left is to identify the two

isolated bands at λ3298.1 (3) and 3323.7 (1) as the other component of the doublet system $^2\Pi - {}^2\Sigma$. These bands are shown in Plate XXIIB, Fig. *c*. As is expected from what is found in the corresponding band systems of CdCl and CdI, this system is fragmentary and occurs on the long wavelength side of the fully developed counterpart component analysed by Wieland. The bands are arranged as hereunder giving a lower state first difference of 234 units which compares well with the ground state vibrational frequency of 230 units which is established from the analysis of the *D*-system.

TABLE III

C-system of CdBr Bands

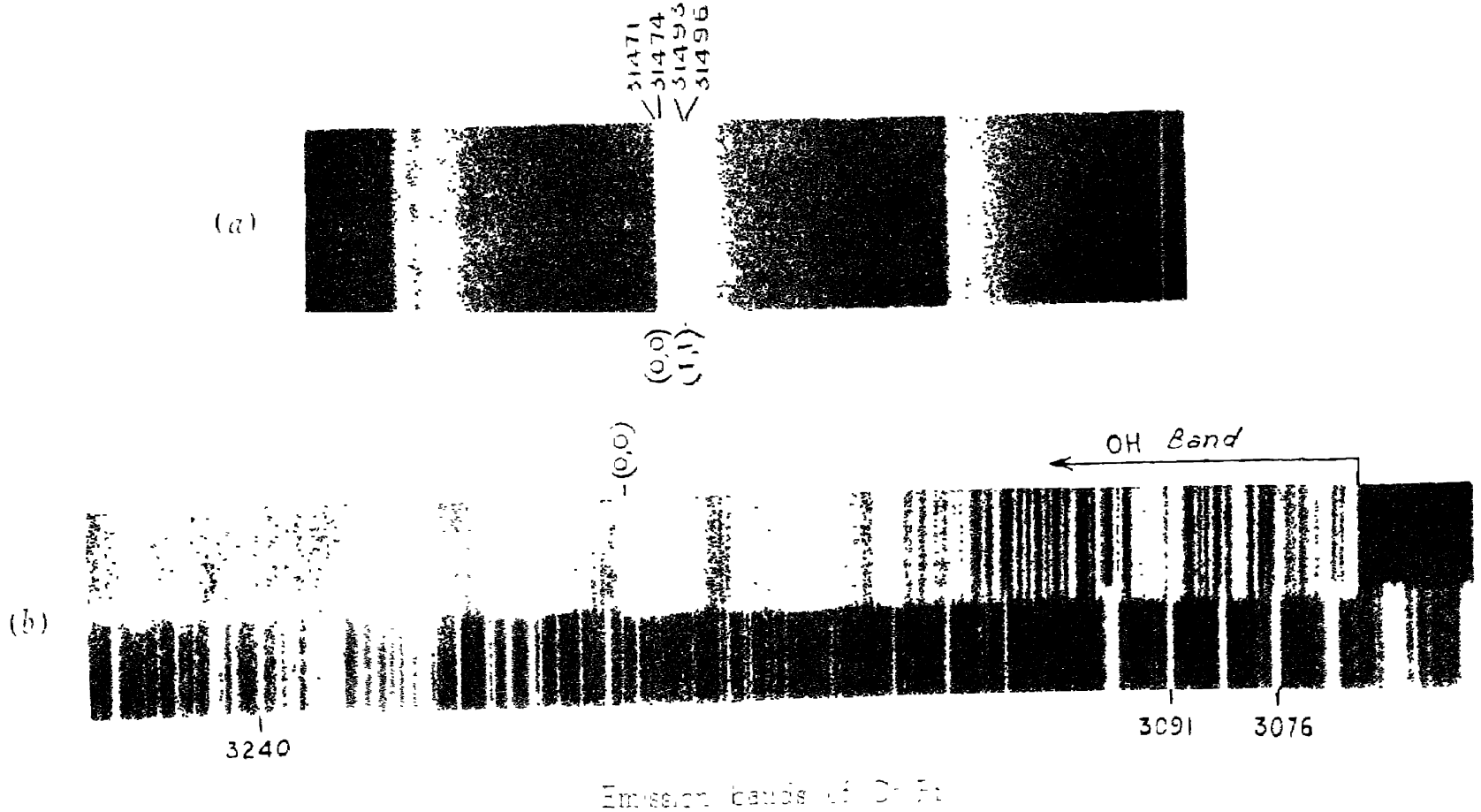
v'' / v'	0		1
0	λ 3298.1 (3)		3323.7 (1)
	ν 30312	234	30078

Further, the separation between the (0,0) band of this system and that of the *D*-system is 31470 − 30312 = 1158 cm.$^{-1}$ which is in such excellent agreement with the predicted 1140 units that one can confidently consider the missing component of the $^2\Pi - {}^2\Sigma$ transition as established.

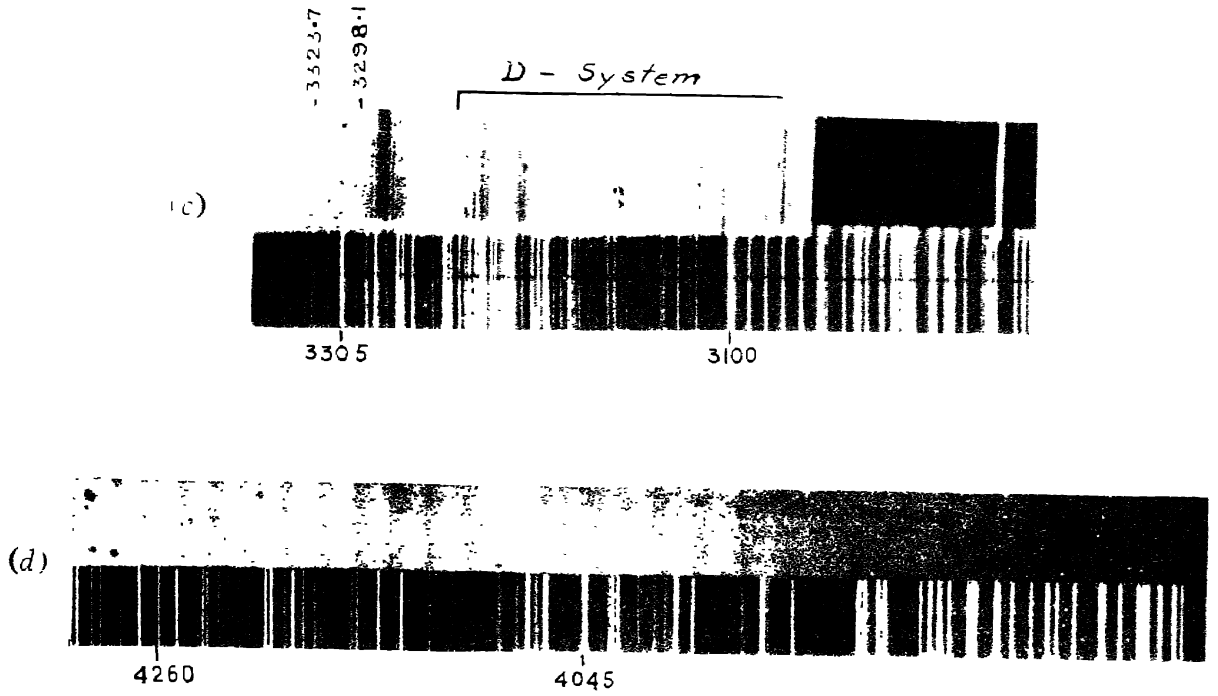
VISIBLE SYSTEM

In none of the investigations on the spectrum of the CdBr molecule are measurements available for the bands in the visible region. In the present work, these bands are photographed on a Fuess glass spectrograph. At higher dispersions the band heads became diffuse. Wavelengths, visual estimates of intensities and wavenumber data of about 50 bands are given in Table IV.

Plate XXIIB, Fig. *d* shows an enlargement of the Fuess spectrogram. The bands are clearly red degraded. The heads are single. They are almost equally spaced. The separation of bands is about 110 cm.$^{-1}$. Assuming that the lower state of the visible bands of CdBr is identical with its ground state ($\omega_e'' = 230$), these bands can be arranged into long progressions. Each progression consists of alternate bands and gives a first difference of about 220 cm.$^{-1}$ for the lower state. These regularities are shown in Table V. If the scheme is correct, there is predissociation in the upper state at $v' = 2$.



Emission bands of C_2H_2



Emission bands of Cd Br

TABLE IV

CdBr Visible Bands

λ	Int.	ν_{vac}	λ	Int	$\nu_{vac.}$
3928.4	r	25448	4355.4	3	22954
			4376.2	3	22844
3944.3	r	25346			
3962.4	2	25230	4398.1	3	22731
			4418.5	3	22626
3978.4	2	25130			
3997.3	2	25010	4478.0	1	22322
			4481.7	3	22307
4013.6	1	24908			
			4484.0	4	22298
4030.6	3	24803	4504.4	5	22194
4048.4	2	24694			
			4525.6	3	22090
4067.2	2	24586	4548.4	5	21979
4085.7	3	24469			
			4570.4	5	21874
4103.2	3	24361	4594.5	4	21758
4121.4	3	24257			
			4613.0	3	21668
4139.8	4	24140	4616.0	3	21644
4158.7	4	24030	4638.0	3	21555
			4643.3	3	21531
4175.6	6	23942			
4195.9	5	23826	4662.0	3	21444
			4680.4	4	21319
4214.2	4	23723			
4234.5	4	23609	4712.4	2	21215
4254.8	3	23496	4733.5	1	21120
4274.2	3	23390	4757.5	1	21014
4294.7	3	23278	4782.7	1	20905
4306.7	3	23213	4807.0	1	20793
4315.0	3	23168	4831.6	1	20691
4335.8	2	23057			

ELECTRONIC STATES.

Four band systems are established in the case of each one of the molecules CdCl and CdI, one in the visible, two in the ultraviolet and one in the far ultraviolet. [Wieland (1929), Howell (1943), Ramasastry and Rao (1946), Ramasastry (1947)]. There is good evidence to consider the two near u.v. systems as due to $^2\Pi - {}^2\Sigma$ transition. The visible system, however, is probably due to $^2\Sigma - {}^2\Sigma$ transition. The corresponding systems of CdBr also can be interpreted accordingly. The far u.v. system of CdCl and CdI have their (0,0) bands at λ2205 and λ2387 respectively. But in the case of CdBr no such band system is obtained in this region of the emission spectrum excepting a continuum from λ2550−λ2500. If, in spite of the disagreement in the region of occurrence, this continuum is supposed to correspond to the far u.v. systems of CdCl and CdI, the difficulty still remains because this upper state of CdBr is repulsive giving rise to continuum

instead of being stable as in CdCl and CdI molecules. In CdF also (Rochester and Olsson, 1939) the corresponding system is not observed but this region of the CdF spectrum is not yet systematically investigated owing to experimental difficulties and in all probability a band sytem of CdF should exist round about $\lambda 2100$. On analogy with Zn halides (Ramasastry, 1948) one more band system is to be expected for cadmium halides also between the far ultra violet and $^2\Pi - ^2\Sigma$ systems. But no definite evidence is as yet available as regards their existence, though about twenty diffuse bands are observed in the expected region (author's unpublished work on CdI). Probably the level is repulsive in Cd halides and one of the observed near u.v. emission continua of CdBr may as well be due to such an unstable level of this molecule.

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